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**MULTILAYER OPTICAL COMPENSATOR, LIQUID CRYSTAL  
DISPLAY, AND PROCESS**

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**MULTILAYER OPTICAL COMPENSATOR, LIQUID CRYSTAL  
DISPLAY, AND PROCESS**

**FIELD OF THE INVENTION**

5                   The present invention relates to a multilayer optical compensator for liquid crystal displays comprising polymeric A and polymeric B layers exhibiting particular birefringent properties. The invention also relates to a process for making such a compensator and liquid crystal displays using the compensator.

10

**BACKGROUND OF THE INVENTION**

                  Liquid crystals are widely used for electronic displays. In these display systems, a liquid crystal cell is typically situated between a pair of polarizer and analyzers. An incident light polarized by the polarizer passes  
15               through a liquid crystal cell and is affected by the molecular orientation of the liquid crystal, which can be altered by the application of a voltage across the cell. The altered light goes into the analyzer. By employing this principle, the transmission of light from an external source, including ambient light, can be controlled. The energy required to achieve this control is generally much less than  
20               required for the luminescent materials used in other display types such as cathode ray tubes (CRT). Accordingly, liquid crystal technology is used for a number of electronic imaging devices, including but not limited to digital watches, calculators, portable computers, electronic games for which light-weight, low-power consumption and long-operating life are important features.

25                   Contrast, color reproduction, and stable gray scale intensities are important quality attributes for electronic displays, which employ liquid crystal technology. The primary factor limiting the contrast of a liquid crystal display (LCD) is the propensity for light to "leak" through liquid crystal elements or cells, which are in the dark or "black" pixel state. Furthermore, the leakage and hence  
30               contrast of a liquid crystal display are also dependent on the direction from which the display screen is viewed. Typically the optimum contrast is observed only within a narrow viewing angle range centered about the normal incidence to the

display and falls off rapidly as the viewing direction deviates from the display normal. In color displays, the leakage problem not only degrades the contrast but also causes color or hue shifts with an associated degradation of color reproduction.

5               LCDs are quickly replacing CRTs as monitors for desktop computers and other office or house hold appliances. It is also expected that the number of LCD television monitors with a larger screen size will sharply increase in the near future. However, unless problems of viewing angle dependence such as coloration, degradation in contrast, and an inversion of brightness are solved,  
10   LCD's application as a replacement of the traditional CRT will be limited.

              A Vertically-Aligned liquid crystal display (VA-LCD) offers an extremely high contrast ratio for normal incident light. FIG. 2A and FIG. 2B are the schematics of VA liquid crystal cell in OFF **201** and ON **203** states. In its OFF state, the liquid crystal optic axis **205** is almost perpendicular to the substrate **207**,  
15   FIG. 2A. With an applied voltage, the optic axis **205** is tilted away from the cell normal, FIG. 2B. In the OFF state, light does not see the birefringence in the normal direction **209**, giving the dark state that is close to that of orthogonally crossed polarizers. However, obliquely propagated light **211** picks up phase retardation giving light leakage. This results in a poor contrast ratio in some  
20   viewing angle range.

              A bend aligned nematic liquid crystal display, also referred as an Optically Compensated Bend Liquid Crystal Display (OCB-LCD) uses a nematic liquid crystal cell based on the symmetric bend state. In its actual operation, the brightness of the display using the bend aligned nematic liquid crystal cell is  
25   controlled by an applied voltage or field that leads to a different degree in the bend orientation within the cell as shown in FIG. 3A (OFF) **301** and FIG.3B (ON) **303**. In both states, the liquid crystal optic axis **305** takes symmetric bend state around the cell middle plane **307**. In the On state, the optic axis becomes substantially perpendicular to the cell plane except near the cell substrates **309**.  
30   OCB mode offers faster response speed that is suitable to the liquid crystal display television (LCD-TV) application. It also has advantages in viewing angle

characteristic (VAC) over conventional displays, such as Twisted Nematic liquid crystal display (TN-LCD)

The above-mentioned two modes, due to their superiority over the conventional TN-LCD, are expected to dominate the high-end application such as LCD-TV. However, practical applications of both OCB and VA-LCDs require optical compensating means to optimize the VAC. In both modes, due to the birefringence of liquid crystal and crossed polarizer, VAC suffers deterioration in contrast when the displays are viewed from oblique angles. Use of biaxial films have been suggested to compensate the OCB (US 6,108,058) and VA (JP1999-95208) LCDs. In both modes, liquid crystals align sufficiently perpendicular to the plane of the cell in ON (OCB) or OFF (VA) states. This state gives positive  $R_{th}$ , thus the compensation films have to have sufficiently large negative  $R_{th}$  for satisfactory optical compensation. The need for a biaxial film with a large  $R_{th}$  is also common for Super Twisted Nematic Liquid Crystal Display (STN-LCD).

Several methods of manufacturing biaxial films with sufficient negative value of  $R_{th}$  suitable for compensating LCD modes such as OCB, VA and STN have been suggested.

US 2001/0026338 discloses a use of retardation increasing agent in combination with triacetylcellulose (TAC). The retardation-increasing agent is chosen from aromatic compounds having at least two benzene rings. By stretching agent doped TAC, one can generate both  $R_{th}$  and  $R_{in}$ . The problems with this method is that the amount of the doping of the agent. To generate the desired effects of increasing  $R_{th}$  and  $R_{in}$ , the necessary amount of agent is high enough to cause coloration. With this method, it is difficult to control the values of  $R_{th}$  and  $R_{in}$  independently.

Sasaki et al. proposes (US2003/0086033) the use of cholesteric liquid crystal disposed on the positively birefringent thermoplastic substrate. The pitch of the cholesteric liquid crystal (CHLC) is shorter than the wavelength of the visible light, thus properly aligned CHLC exhibits form birefringence giving negative  $R_{th}$ .  $R_{in}$  is controlled by adjusting the stretching amount of the thermoplastic substrate. The method enables one to adjust  $R_{th}$  and  $R_{in}$  separately.

However, the use of short pitch CHLC not only makes the manufacturing cost high but also complicates the processing due to the alignment procedure.

JP2002-210766 discloses the use of propionyl or butyryl substituted TAC. They show higher birefringence than ordinary TAC. Thus, by  
5 biaxially stretching the substituted TAC film, one generates  $R_{in}$  and  $R_{th}$ . The method does not require any additional coating or layer but it suffers a difficulty of independent control of  $R_{in}$  and  $R_{th}$ .

Thus, it is a problem to be solved to provide a multilayer optical compensator with independently controlled  $R_{th}$  and  $R_{in}$  that can be readily  
10 manufactured.

### SUMMARY OF THE INVENTION

The invention provides a multilayer compensator comprising one or more polymeric A layers and one or more polymeric B layers, wherein said A layers comprise a polymer having an out-of-plane birefringence not more negative than -0.01, and said B layers comprise an amorphous polymer having an out-of-plane birefringence more negative than -0.01, and the overall in-plane retardation ( $R_{in}$ ) of said multilayer compensator is greater than 20nm and the out-of-plane retardation ( $R_{th}$ ) of said multilayer compensator is more negative than -20nm. The invention also provides a LCD and a process for preparing a compensator of the invention.

The invention multilayer optical compensator is readily manufactured and provides the required value of the  $R_{in}$  and the  $R_{th}$  values.

### 15 BRIEF DESCRIPTION OF THE DRAWINGS

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter of the present invention, it is believed that the invention will be better understood from the following description when taken in conjunction with the accompanying drawings, wherein:

20 FIG.1 is a view of a typical layer with thickness  $d$  and x-y-z coordinate system attached to the layer.

FIG.2A and FIG. 2B are schematics showing, respectively, the typical ON and OFF state of the VA liquid crystal cell.

FIG. 3A and FIG. 3B are schematics showing, respectively, the typical ON and OFF states of the OCB liquid crystal cell.

FIG. 4A, FIG. 4B and FIG. 4C are elevation schematics of the multilayer optical compensator of the invention.

5 FIG. 5A, FIG. 5B and FIG. 5C are schematics of a liquid crystal display with multilayer optical compensators of the invention.

### DETAILED DESCRIPTION OF THE INVENTION

The following definitions apply to the description herein:

10 Optic axis refers to the direction in which propagating light does not see birefringence.

ON and OFF state refers to the state with and without applied voltage to the liquid crystal cell.

In-plane phase retardation,  $R_{in}$ , of a layer **101** shown in FIG. 1 is a quantity  
15 defined by  $(n_x - n_y)d$ , where  $n_x$  and  $n_y$  are indices of refraction in the direction of  $x$  and  $y$ . The  $x$  axis is taken as a direction of maximum index of refraction in the  $x$ - $y$  plane and the  $y$  direction is perpendicular to the  $x$  axis. For stretched positively birefringent layers,  $x$  corresponds to the direction of primary stretch. The  $x$ - $y$  plane is parallel to the plane **103** of the layer.  $d$  is a thickness of the layer in the  $z$ -  
20 direction. The quantity  $(n_x - n_y)$  is referred to as in-plane birefringence,  $\Delta n_{in}$ . The values of  $\Delta n_{in}$  and  $R_{in}$  hereafter are given at wavelength  $\lambda = 550\text{nm}$ .

Out of-plane phase retardation,  $R_{th}$ , of a layer **101** shown in FIG. 1, herein, is a quantity defined by  $[n_z - (n_x + n_y)/2]d$ .  $n_z$  is the index of refraction in  $z$ -direction. The quantity  $[n_z - (n_x + n_y)/2]$  is referred to as out-of-plane birefringence,  $\Delta n_{th}$ . If  
25  $n_z > (n_x + n_y)/2$ ,  $\Delta n_{th}$  is positive, thus the corresponding  $R_{th}$  is also positive. If  $n_z < (n_x + n_y)/2$ ,  $\Delta n_{th}$  is negative and  $R_{th}$  is also negative. The values of  $\Delta n_{th}$  and  $R_{th}$  hereafter are given at  $\lambda = 550\text{nm}$ .

Intrinsic Birefringence  $\Delta n_{int}$  of a polymer herein refers to the quantity defined by  $(n_e - n_o)$ , where  $n_e$ , and  $n_o$  are extraordinary and ordinary index of the polymer,  
30 respectively. Intrinsic birefringence is determined by factors, such as the polarizabilities of functional groups and their bond angles with respect to the

polymer chain. The actual birefringence (in-plane  $\Delta n_{in}$  or out-of-plane  $\Delta n_{th}$ ) of a polymer layer depends on the process of forming it, thus the order parameter, and the  $\Delta n_{int}$ .

5 Amorphous means a lack of long-range order. Thus an amorphous polymer does not show long-range order as measured by techniques such as X-ray diffraction.

Chromophore means an atom or group of atoms that serve as a unit in light adsorption. (*Modern Molecular Photochemistry* Nicholas J. Turro Editor, Benjamin/Cummings Publishing Co., Menlo Park, CA (1978) Pg 77). Typical chromophore groups include vinyl, carbonyl, amide, imide, ester, carbonate, aromatic (i.e. heteroaromatic or carbocyclic aromatic such as phenyl, naphthyl, biphenyl, thiophene, bisphenol), sulfone, and azo or combinations of these groups.

10 Non-visible chromophore means a chromophore that has an absorption maximum outside the range of 400-700nm.

Contiguous means that articles are in contact with each other. In two contiguous layers, one layer is in direct contact with the other. Thus, if a polymer layer is formed on the substrate by coating, the substrate and the polymer layers are contiguous.

The invention provides a multilayer compensator comprising one or more polymeric A layers and one or more polymeric B layers, wherein said A layers comprises a polymer having an out-of-plane birefringence not more negative than -0.01, and said B layer comprises an amorphous polymer having an out-of-plane birefringence more negative than -0.01, and the overall in-plane retardation ( $R_{in}$ ) of said multilayer compensator is greater than 20nm and the out-of-plane retardation ( $R_{th}$ ) of said multilayer compensator is more negative than -20nm. The A layer is made from polymer film other than one containing a chromophore group in the backbone. The A layer has positive intrinsic birefringence,  $\Delta n_{int}$ . Examples of such a polymer include, TAC, cellulose acetate butylate (CAB), cyclic polyolefin, polycarbonate, polysulfonate, and other polymers known to those skilled in the art. These polymeric materials can be made into a film form by solvent casting, heat extrusion, or other methods. To generate  $R_{in}$  that is greater than 20nm in the A layer, any viable methods can be used, however, most commonly practiced procedure is stretching. As the A layers

are made from polymer film with positive  $\Delta n_{\text{int}}$ , indices of refraction in the plane of the layer satisfies  $n_x > n_y$ , where “x” denotes the primary direction of stretching and “y” is the direction perpendicular to x. By stretching polymeric materials, individual polymer chain segments are oriented predominantly to the direction of primary stretch, thus increase the birefringence of polymer layer. As it is necessary to orient the polymer segment, the stretching has to be done above the glass transition temperature of the polymeric materials. Thus, the polymeric film is heated above  $T_g$  and stretched. Other method is to stretch the film while solvents are incorporated within the film. With this method, the film can be stretched immediately after the polymer is solvent-cast into a film form. The film can be stretched uniaxially or biaxially. In uniaxial stretching, the film is stretched into one direction. However, by uniaxial stretching, it is difficult to control the films three indices of refraction,  $n_x$ ,  $n_y$  and  $n_z$ , where  $n_z$  is an index of refraction in the film normal direction. This is particularly true when the stretching of the film in the x direction is large enough so that there is a contraction in the y direction. This contraction effectively gives stretching in the film normal direction z, thus increases  $n_z$ . In biaxial stretching, where two stretching directions x and y are perpendicular to each other, the undesired shrinkage caused by the stretch in the primary stretching direction (say in x direction) is prevented by simultaneous stretch in the secondly direction (y). Thus the increase in  $n_z$  can effectively be prevented. Means to stretch are not particularly limited so long the stretched film has sufficient uniformity in three indices of refraction. The polymeric A layer has  $\Delta n_{\text{th}}$  not more negative than  $-0.01$ . The polymeric A layers of the multilayer compensator are such that the overall in-plane retardation ( $R_{\text{in}}$ ) of said multilayer compensator is suitably greater than 20nm, desirably between than 30 and 200nm, and conveniently between 30nm and 150nm.

The polymeric B layers will typically be solvent coated onto the A layer. This solvent coating could be accomplished by spin coating, hopper coating, gravure coating, wire bar coating or other coating methods known to those skilled in the art. The coated B layers are contiguous to the A layer.



The B layer is coated from a solution containing a polymer that yields high negative birefringence that is more negative than  $-0.01$  upon solvent coating. To produce negative  $\Delta n_{th}$  (or  $R_{th}$ ), polymers with positive  $\Delta n_{int}$  are used. Such polymers usually contain non-visible chromophore groups such as vinyl,  
5 carbonyl, amide, imide, ester, carbonate, sulfone, azo, and aromatic groups (i.e. benzene, naphthalate, biphenyl, bisphenol A) in the polymer backbone. Examples of such polymers are polyesters, polycarbonates, polyimides, polyetherimides, and polythiophenes. One could also add fillers and non-polymeric molecules to these polymers for the second layer.

- 10 Desirably, polymers to be used in the B layers will not have chromophores off of the backbone. An example of such an undesirable polymer with chromophores in and off the backbone would be polyarylates possessing the fluorene group. The glass transition temperature ( $T_g$ ) of the polymers used in the B layer is significant. It should be above  $180^\circ\text{C}$  to achieve the desired results.
- 15 The polymers used in the B layers could be synthesized by a variety of techniques: condensation, addition, anionic, cationic or other common methods of synthesis could be employed.

- The thickness of each B layer should be less than  $30\mu\text{m}$ . Typically it should be from  $0.1\mu\text{m}$  to  $20\mu\text{m}$ . Conveniently it should be from  $1.0\mu\text{m}$  to  
20  $10\mu\text{m}$ . Desirably it should be from  $2\mu\text{m}$  to  $8\mu\text{m}$ .

The combined thickness of the multilayer optical compensator should be less than  $200\mu\text{m}$ . Typically it should be from  $40\mu\text{m}$  to  $150\mu\text{m}$ . Desirably it should be from  $80\mu\text{m}$  to  $110\mu\text{m}$ .

- The B layers should be of sufficient thickness so that the  
25 out-of-plane retardation of the B layers is more negative than  $-20\text{nm}$ . Typically it should be from  $-600\text{nm}$  to  $-60\text{nm}$ . Conveniently it should be from  $-500\text{nm}$  to  $-50\text{nm}$ . Desirably it should be from  $-400\text{nm}$  to  $-50\text{nm}$ .

- Reference will now be made to the drawings in which the various elements of the present invention will be given numerical designations and in  
30 which the invention will be discussed so as to enable one skilled in the art to make

and use the invention. It is to be understood that elements not specifically shown or described may take various forms well known to those skilled in the art.

FIG. 4A, FIG. 4B and FIG. 4C are elevation schematics of the exemplary multilayer optical compensators in accordance with the invention.

5 Compensator **401** in FIG. 4A has a structure in which a B layer **409** is disposed on an A layer **407**. The A layer **407** and the B layer **409** are contiguous. It is also possible to have two B layers **413**, **415** disposed on one A layer **411** such as the compensator **403** in FIG. 4B. In other case **405**, one B layer **417** is sandwiched by two A layers **419**, **421**. The compensator **405** can be formed, for example, by  
10 laminating contiguous layers of A **421** and B **417**, and the single layer of A **419**. The lamination is done at the interface of B layer **417** and A layer **419**, and the two layers **417** and **419** may or may not be contiguous depending on the method of the lamination. One skilled in the art could conceive of more complex structures.

15 In LCD **501** shown in FIG. 5A, the liquid crystal cell **503** is placed between the polarizer **505** and analyzer **507**. Transmission axis of the polarizer **509** and analyzer **511** form angle  $90 \pm 10^\circ$  thus, pair of polarizer **509** and analyzer **511** are said to be "crossed polarizer". A multilayer optical compensator **512** is placed between the polarizer **505** and the liquid crystal cell **503**. It can also be  
20 placed between the liquid crystal cell **503** and the analyzer **507**. LCD **513** shown schematically in FIG. 5B has two multilayer optical compensators **515**, **517** placed on the both sides of the liquid crystal cell **503**. FIG. 5C shows an application example of multilayer optical compensator in a reflective type LCD **519**. The liquid crystal cell **503** is located between the polarizer **505** and a reflective plate  
25 **521**. In the figure, the multilayer compensator **523** is placed between the liquid crystal cell **503** and the polarizer **505**. However, it can also be placed between the reflective plate **521** and the liquid crystal cell **503**.

Compared to the prior art, embodiments of the present invention avoids retardation increasing agent that causes coloration, do not require the use  
30 of liquid crystal compounds and its alignment procedure, provide enhanced optical compensation in a relatively thin ( $<200\mu\text{m}$ ) structure, and are easily manufactured.

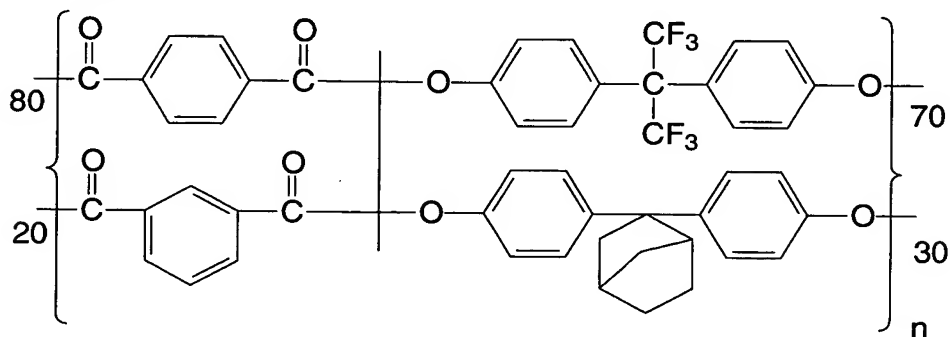
As a further attribute, embodiments enable the control of  $R_{in}$ , which is primarily the responsibility of the A layer while control of  $R_{th}$  is primarily the responsibility of the B layer. In the prior art,  $R_{in}$  and  $R_{th}$  are often coupled and are not controlled independently.

5 The present invention is further illustrated by the following non-limiting examples of its practice.

**Example:**

**Polymer 1 (synthesis):**

10 To a stirred mixture of 4,4'-hexafluoroisopropylidenediphenol (23.53 g, 0.07 mole), 4,4'-(2-norbornylidene) bisphenol (8.4 g, 0.03 mole) and triethylamine (22.3 g, 0.22 mole) in methyl ethyl ketone (100 mL) at 10° C. was added a solution of terephthaloyl chloride (16.23 g, 0.8 mole) and isophthaloyl chloride (4.08g, 0.2 mole) in methyl ethyl ketone (60 mL). After the addition, the  
15 temperature was allowed to rise to room temperature and the solution was stirred under nitrogen for 4 hours, during which time triethylamine hydrochloride precipitated in a gelatinous form and the solution became viscous. The solution was then diluted with toluene (160 mL) and washed with dilute hydrochloric acid, (200 mL of 2% acid) followed three times by water (200 mL). The solution was  
20 then poured into ethanol with vigorous stirring, and a white bead like polymer precipitated, collected and dried at 50° C. under vacuum for 24 hours. The glass transition temperature of this polymer was measured by differential scanning calorimetry to be 265° C



25 Poly(4,4'-hexafluoroisopropylidene-bisphenol-co- 4,4'-(2-norbornylidene) bisphenol) terephthalate-co-isophthalate.

Polymer 1

Polymer 1 was spun cast (8% solids in 80% propylacetate 20% toluene) onto both a glass slide and a stretched polymer substrate sample, and was analyzed with an ellipsometer (model M2000V, J.A. Woollam Co.) at 550nm wavelength to obtain the  $R_{th}$  and  $R_{in}$ . These values are listed in TABLE I.

TABLE I

<u>Sample</u>	$R_{in}$ (nm)	$R_{th}$ (nm)
<b>Polymer 1 on glass</b>	<b>0.6</b>	<b>-38</b>
<b>Stretched polymer substrate</b>	<b>40.0</b>	<b>-123</b>
<b>Polymer A on stretched polymer substrate</b>	<b>35.0</b>	<b>-190</b>

The layer of polymer 1 also did not show any sign of a long-range order therefore the layer was determined to be comprised of an amorphous polymer.

**PARTS LIST**

<b>101</b>	film
<b>103</b>	plane of the film
<b>201</b>	VA liquid crystal cell in OFF state
<b>203</b>	VA liquid crystal cell in ON state
<b>205</b>	liquid crystal optic axis
<b>207</b>	liquid crystal cell substrate
<b>209</b>	light propagating cell normal direction
<b>211</b>	light propagating oblique direction
<b>301</b>	OCB liquid crystal cell in OFF state
<b>303</b>	OCB liquid crystal cell in ON state
<b>305</b>	liquid crystal optic axis
<b>307</b>	cell middle plane
<b>309</b>	cell boundaries
<b>401</b>	multilayer optical compensator
<b>403</b>	multilayer optical compensator
<b>405</b>	multilayer optical compensator
<b>407</b>	A layer
<b>409</b>	B layer
<b>411</b>	A layer
<b>413</b>	B layer
<b>415</b>	B layer
<b>417</b>	B layer
<b>419</b>	A layer
<b>421</b>	A layer
<b>501</b>	LCD
<b>503</b>	liquid crystal cell
<b>505</b>	polarizer
<b>507</b>	analyzer
<b>509</b>	transmission axis of polarizer
<b>511</b>	transmission axis of analyzer
<b>512</b>	multilayer optical compensator

<b>513</b>	LCD
<b>515</b>	multilayer optical compensator
<b>517</b>	multilayer optical compensator
<b>519</b>	LCD
<b>521</b>	reflective plate
<b>523</b>	multilayer optical compensator
$n_x$	index of refraction in x direction
$n_y$	index of refraction in y direction
$n_z$	index of refraction in z direction
$n_o$	ordinary index of refraction
$n_e$	extraordinary index of refraction
$\Delta n_{th}$	out-of-plane birefringence
$\Delta n_{in}$	in-plane birefringence
$\Delta n_{int}$	intrinsic birefringence of polymer
$d$	thickness of the layer or film
$R_{th}$	out-of-plane phase retardation
$R_{in}$	in-plane phase retardation
$\lambda$	wavelength
$T_g$	glass transition temperature